*Acta Cryst.* (1960). **13**, 507

## Structure of chromium(III) fluoride.

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(*Received* 30 *November* 1959 *and in revised form* 11 *January* 1960)

In the extensive series of trifluorides studied by Jack *et al.* (Gutmann & Jack, 1951; Jack & Gutmann, 1951; Hepworth, Jack, Peacock & Westland, 1957; Hepworth & Jack, 1957; Jack & Maitland, 1957) the structure of chromium trifluoride was shown to be their $VF_3$ type. The author was unaware of this result before undertaking a refinement of the approximate result, with a slightly different value for the fluoride parameter, obtained from neutron diffraction by Wollan, Child, Koehler & Wilkinson (1958). The purpose of this note is mainly to report agreement with the X-ray result of Jack & Maitland (1957).

The refinement was based on Norelco diffractometer powder intensities with Cu $K\alpha$ radiation (semi-quantitative comparison of these intensities with those of Debye–Scherrer photographs showed preferred orientation to be inappreciable). The intensities were obtained from the areas measured with a planimeter, of several recordings at different amplification of the diffractometer traces with suitable estimation of back-ground. In addition the space group was verified by Buerger precession camera photography of a single crystal grown by H. Guggenheim of these Laboratories. Long exposures showed the rhombohedral and glide plane extinctions to be indeed present, giving as most probable space groups $C_{3v}^6$–$R3c$ and $D_{3d}^6$–$R\bar{3}c$; in the absence of further information the centrosymmetric latter is chosen, as was done by Jack & Maitland (1957). The lattice constants were determined photographically using Cr $K\alpha$ radiation; at 300 °C. they were obtained using the camera of Bond (1958). Higher temperature photography was attempted, but the back reflection lines became weak and broad so that the lattice constants could not be obtained with any accuracy.

In $D_{3d}^6$–$R\bar{3}c$ there are

$$2\ \mathrm{Cr\ in}\ (b),\ (0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}),\ \mathrm{and}$$

$$6\ \mathrm{F\ \ in}\ (e),\ \pm(x, \tfrac{1}{2}-x, \tfrac{1}{4}\circlearrowright)\ .$$

Using the scattering factors for Cr(III) obtained by extrapolation of the values of Thomas & Umeda (1957) and for $F^-$ from Berghuis *et al.* (1955) together with the real and imaginary parts of the dispersion corrections of Dauben & Templeton (1955), intensities were calculated in the usual way. By trial and error, the minimum in the function $|kI_o-I_c|$, using the observed reflections only and excluding 110 which is strong and subject to large errors was found to occur at $x_F=-0{\cdot}137$, $B_{Cr}=B_F=0{\cdot}37$. The structural results are collected in Table 1.

The observed and calculated $d$-spacings (obs. Cr $K\alpha$) and relative intensities (Cu $K\alpha$) are given in Table 2.

Table 1. *Structure of* $CrF_3$

| $a$ (Å) | $\alpha$ (°) | $x_F$ | Ref. |
|---|---|---|---|
| 5·2643 ± 0·0003 | 56·563 ± 0·005 | −0·136 ± 0·003 | 1 |
| — | — | −0·12 ± 0·02 | 2 |
| 5·264 ± 0·001 | 56·609 ± 0·006 | −0·137 ± 0·002 | 3 |
| 5·332 (300 °C.) | 56·61 (300 °C.) | — | 4 |

1 Jack & Maitland (1957)
2 Wollan *et al.* (1958)
3 This work
4 This work

Table 2. *Observed and calculated X-ray data for* $CrF_3$

Observed $d$-spacings Cr $K\alpha$. $a=5{\cdot}264$. $\alpha=56{\cdot}609°$
Relative intensities Cu $K\alpha$. Rhombohedral indices

| $hkl$ | $d_o$ | $d_c$ | $I_o$ | $I_c$ | |
|---|---|---|---|---|---|
| 110 | 3·599 | 3·618 | 412 | 487 | |
| 211 | 2·614 | 2·625 | 90 | 94 | |
| $10\bar{1}$ | 2·488 | 2·496 | 35 | 32 | |
| 222 | — | 2·203 | — | 0·7 | |
| 210 | 2·165 | 2·172 | 121 | 104 | |
| 200 | 2·050 | 2·054 | 24 | 22 | |
| 220 | 1·806 | 1·809 | 92 | 90 | |
| 321 | 1·649 | 1·651 | 116 | 131 | |
| $20\bar{1}$ | 1·619 | 1·622 | 8 | 8 | |
| $21\bar{1}$ | 1·584 | 1·586 | 62 | 59 | |
| 332 | 1·540 | 1·543 | 15 | 18 | |
| 310 | 1·463 | 1·464 | 42 | 40 | |
| $2\bar{1}\bar{1}$ | 1·440 | 1·441 | 56 | 50 | |
| 320 | 1·388 | 1·390 | 6 | 4 | |
| 422 | 1·3114 | 1·3125 | 24 | 25 | |
| 432 | 1·2639 | 1·2656 | 26 | 10 | 26 |
| 433 | | 1·2638 | | 16 | |
| $20\bar{2}$ | 1·2474 | 1·2480 | 8 | 8 | |
| 421 | — | 1·2355 | — | 2 | |
| 411, 330 | 1·2009 | 1·2059 | 13 | 4 | 8 |
| $31\bar{1}$ | | 1·2007 | | 4 | |
| $21\bar{2}$ | 1·1941 | 1·1941 | 4 | 5 | |
| $30\bar{1}$ | 1·1797 | 1·1798 | 35 | 32 | |
| 431 | 1·1616 | 1·1617 | 15 | 17 | |
| 442 | Cr $K\alpha$ | 1·1275 | 15 | 4 | 12 |
| $32\bar{1}$ | cut off | 1·1271 | | 8 | |
| 444 | | 1·1013 | 8 | 8 | |
| 410 | | 1·0919 | 4 | 3 | |
| 420 | | 1·0858 | 20 | 20 | |
| $22\bar{2}$ | | 1·0666 | 10 | 10 | |
| 532 | | 1·0275 | 16 | 13 | 17 |
| 400 | | 1·0272 | | 4 | |
| 430 | | 1·0121 | — | 3 | |
| 543 | | 1·0075 | — | 6 | |
| $30\bar{2}$ | | 0·9890 | — | 0·5 | |
| $31\bar{2}$ | | 0·9808 | 5 | 5 | |
| 521 | | 0·9704 | 9 | 6 | 7 |
| 542 | | 0·9679 | | 1 | |
| 531 | | 0·9509 | 24 | 2 | 24 |
| $41\bar{1}$ | | 0·9499 | | 22 | |
| $3\bar{1}\bar{2}$ | | 0·9434 | 10 | 8 | |
| 421 | | 0·9286 | — | 0·4 | |
| $40\bar{1}$, $32\bar{2}$ | | 0·9225 | 11 | 1 | 8 |
| 554 | | 0·9222 | | 7 | |
| 440 | | 0·9044 | — | 4 | |
| 541 | | 0·8880 | 17 | 19 | |
| 520 | | 0·8780 | — | 0·0 | |
| 633, 552 | | 0·8750 | 22 | 27 | |
| 510, $43\bar{1}$ | | 0·8672 | 40 | 35 | 39 |
| 644 | | 0·8650 | | 3 | |
| 643 | | 0·8631 | | 1 | |
| $4\bar{1}\bar{1}$ | | 0·8573 | — | 1 | |
| 530 | | 0·8503 | 25 | 25 | 27 |
| 632 | | 0·8487 | | 2 | |

Table 2 (*cont.*)

| *hkl* | $d_c$ | $I_o$ | $I_c$ | |
|---|---|---|---|---|
| 622 | 0·8366 | 26 | 10 | 29 |
| $33\bar{2}$ | 0·8365 | | 19 | |
| $30\bar{3}$ | 0·8320 | 12 | 10 | 14 |
| 654 | 0·8308 | | 4 | |
| 642 | 0·8257 | 17 | 11 | |
| $41\bar{2}$ | 0·8175 | 17 | 1 | 22 |
| 653 | 0·8174 | | 17 | |
| $31\bar{3}$ | 0·8155 | | 4 | |
| 655 | 0·8113 | 34 | 7 | 36 |
| $40\bar{2}$ | 0·8108 | | 29 | |
| 621, 540 | 0·7937 | 26 | 1 | 24 |
| 631 | 0·7933 | | 10 | |
| $42\bar{2}$ | 0·7931 | | 13 | |

In this structure, each Cr(III) with point symmetry $C_{3i}-\bar{3}$ is surrounded by 6 $F^-$ at 1·90 Å with a Cr–F–Cr angle between octahedra of 146°. The octahedra of $F^-$ around Cr(III) are perfectly regular within experimental error since the calculated F–Cr–F angles are 89·7° and 90·3°.

At 300 °C. it is seen that the situation for $CrF_3$ is similar to that found in the rare earth aluminates by Geller & Bala (1956); i.e., *a* elongates with rising temperature faster than α increases, so that the transition to cubic for $CrF_3$, if it ever occurs below the melting point, should take place at a very high temperature.

It is of interest to compare this structure with the neutron-diffraction results on magnetic spin alignment. The results of Wollan *et al.* (1958) show that the magnetic space group is No. 89–$C2'/c'$ (the notation used is that of Belov, Neronova & Smirnova, 1957) in which the magnetic moments are allowed to move toward one another out of perfect antiparallel alignment without destroying the symmetry. Thus, 'weak' ferromagnetism of the type discussed by Dzialoshinskii (1957*a*, *b*) is allowed, and it was observed in the magnetization curve obtained by Bozorth & Kramer (1958) in collaboration with the author. It has also been seen by Henry, Griffel & Hansen (1955) and by Hansen (1959), who, however, attribute the spontaneous magnetization to ferrimagnetism.

The author is grateful to S. Geller for many helpful discussions. Thanks are also due R. G. Treuting for the use of and assistance with his IBM 704 programs, D. W. Mitchell, W. Masterson, and C. E. Miller for help with the experimental work.

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*Acta Cryst.* (1960). **13**, 508

## Structure factor slide rule.

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(*Received* 22 *January* 1960)

Structure factor contributions of the product type,

$$F_n = f_n \cdot \frac{\sin}{\cos}(hx_n) \cdot \frac{\sin}{\cos}(ky_n) \cdot \frac{\sin}{\cos}(lz_n)$$

can be calculated conveniently by means of the device illustrated in Fig. 1. It is a composite slide rule consisting of three cyclometric scales, each covering one quarter of a period, of a straight logarithmic one for reading the product, and of a movable stage carrying a graph of $\log f_n$ *vs.* $\sin^2\theta$. The width of this stage is limited to the relative range of variation of the atomic scattering factors likely to be employed, usually less than one and a half decade. For atoms of strongly differing scattering power, the *f*-graphs can be brought to scale by shifting the overall zero point of the calculator.

The sign of the composite product is indicated by colour signals coupled with the cyclometric scales: the numbering of these scales is divided into four groups, printed on a white or red base according to the sign of the function. The number strips are mounted, as shown in Fig. 2, on a holder carrying a hinged flap. The whole array rests in a groove in the scale carrier; the transition from sine to cosine numbering is effected by simply inverting it in this groove.—As will be apparent from